(12) UK Patent Application (19) GB (11) 2 349 388 (13) A

(43) Date of A Publication 01.11.2000

(21) Application No 0009403.7

(22) Date of Filing 18.04.2000

(30) Priority Data
(31) 11117929 (32) 26.04.1999 (33) JP

(71) Applicant(s)
Fuji Electric Co Ltd
(Incorporated in Japan)
1-1 Tanabeshinden, Kawasaki-ku, Kawasaki-shi,
Kanagawa 210-0856, Japan

(72) Inventor(s)
Ryoji Kobayashi
Yotaro Shiraishi
Koji Kawaguchi

(74) Agent and/or Address for Service
G F Redfern & Co
Redfern House, 149/151 Tarring Road, WORTHING,
West Sussex, BN11 4HE, United Kingdom

(51) INT CL^7
C08K 5/3417 , G02B 5/20 , H05B 33/12

(52) UK CL (Edition R)
C3K KAA K334 K336 K402
C3V VBC
C3W W209 W304C
U1S S1411 S1918 S1927 S2285 S3018

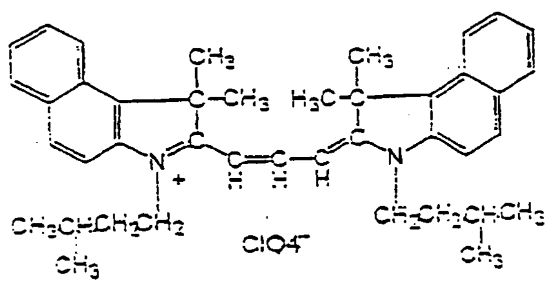
(56) Documents Cited
GB 2313921 A EP 0723167 A2 EP 0387715 A2

(58) Field of Search
UK CL (Edition R) C3K KAA , C3V VBC
INT CL^7 C08K 5/00 5/3417 , C09B 57/00 , C09K 11/06 , G02B 5/20 , H05B 33/12
ONLINE: CAS-online, EPODOC, JAPIO, WPI

(54) Abstract Title

Blue colour filter and electroluminescent device

(57) The blue colour filter includes a photosensitive resin; and a dye containing at least a cyanine dye describe by the following structural formula (1).



(1)

The organic EL device including the blue colour filter includes a glass substrate 1, a blue colour filter 2, an organic protection layer 3, an inorganic oxide layer 4, and an organic light-emitting layer including an anode 5a, a hole injection layer 5b, a hole transport layer 5c, a light emitting layer 5d, an electron injection layer 5e, and a cathode 5f.

Further cyanine dyes may also be included in the filter.

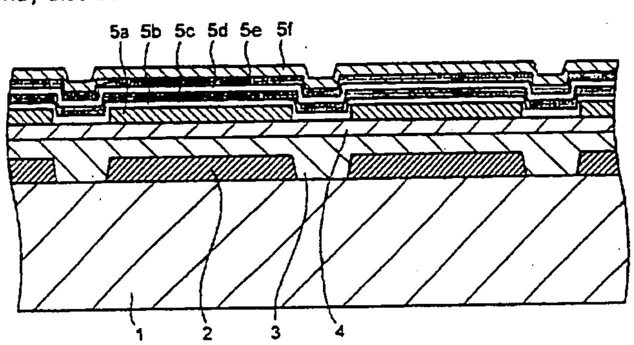


FIG. 1

GB 2 349 388 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

BLUE COLOUR FILTER AND ORGANIC ELECTROLUMINESCENT DEVICE USING THE SAME

The present invention relates to a blue colour filter that includes a dye or a pigment. The present invention also relates to a blue colour filter that is used typically in combination with an organic electroluminescent element (hereinafter referred to as an EL element).

Research and development of various display devices have been explored vigorously to meet the increasing demands for flat panel displays substituting for the conventional cathode ray tubes (CRTs). Electroluminescent elements (EL elements) have been investigated and developed as all-solid-state and self-light-emitting devices which meet the foregoing demands. The EL elements have attracted much attention due to the high definition and high visibility, which the other display devices do not exhibit.

Various measures have been proposed for providing the flat panel displays with polychromatic-display function or full-colour-display function. Japanese Unexamined Laid Open Patent Applications S57-157487, S58-147989 and H03-214593 disclose flat panel displays which arrange light emitters for the three primary colours, i.e. green-light emitters, blue-light emitters and red-light emitters, in a matrix and make the light emitters for the respective colours emit light independently. For applying an organic EL element to this type of flat panel display, it is necessary to precisely and finely arrange three kinds of light emitting materials for the respective three primary colours in a matrix. However, it is difficult to precisely and finely arrange three kinds of light emitting materials in a matrix with reduced manufacturing costs. Since the lives of the three kinds of light emitters are different from each other, chromaticity deviations are caused with elapse of time. The x-value and the y-value on the CIE chromaticity coordinate for the reported blue organic EL device are 0.16 and 0.15, respectively (cf. Japanese Unexamined Laid Open Patent Application H08-286033). If one compares the CIE chromaticity coordinate for the reported blue organic EL device with the NTSC hue (that is a hue of the standard blue for the CRTs corresponding to x=0.14 and y=0.08 on the CIE chromaticity coordinate), it is obvious that the blue colour from the reported blue organic EL device is not pure enough.

Patent Application H01-5273). The coating film obtained by the dying method has some problems in its weather resistance, thermal resistance and moisture resistance. By the printing method, a colour filter is formed by printing ink obtained by dispersing a pigment in a thermosetting resin or in a ultraviolet-ray-curing resin (cf. Japanese Unexamined Laid Open Patent Applications S62-54774 and S63-129303). The flatness and smoothness of the printed ink film surface pose certain problems for precisely positioning the colour filter patterns for the three primary colours.

Colour filters manufactured by the pigment dispersion method are used mainly to meet the thermal resistance required for the manufacturing process of colour displays, to meet the weather resistance required for using the displays and to meet the precision and fineness required for displaying images.

In the pigment dispersion method, a photosensitive resin solution, thereinto small grains of 1 μm or less in diameter of a red pigment, a blue pigment or a green pigment are dispersed, is coated on a glass substrate, and the coated photosensitive resin film is patterned by photolithography to form a desired pixel pattern (cf. Japanese Examined Patent Application H04-37987 and H04-39041).

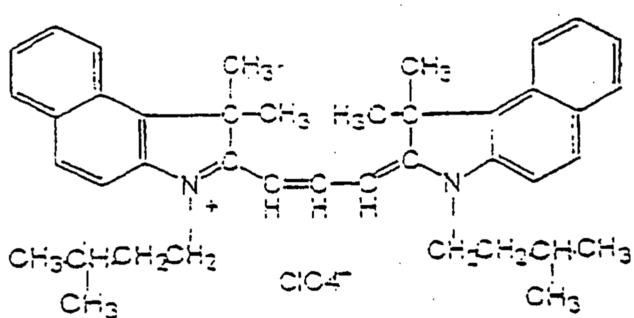
Recently it has been required for the colour displays to arrange pixels precisely and finely, to display images with full colours and to reduce power consumption. Most part of the electric power for operating the colour display is consumed by the back light for displaying. To meet these demands, it is necessary to improve the colour purity, the chroma and the light transmission amount of the colour filter. To increase the light transmission amount through the colour filter, the content of the pigment with respect to the photosensitive resin in the material for image formation or the film thickness of the pixels formed of the materials for image formation has been reduced.

However, these methods for increasing the light transmission amount through the colour filter reduces the chroma of the colour filter. The reduced chroma of the colour filter impairs the brightness of the colours necessary for displaying, causing whitened images including the background. When the colouring pigment content is increased so as not to impair the chroma of the colour filter, displayed images including the

A colour filter that uses a pigment mixture containing copper phthalocyanine blue and dioxazine violet has been proposed (cf. Japanese Examined Patent Application H06-95211, Japanese Unexamined Laid Open Patent Application H01-200353 and Japanese Examined Patent Application H04-37987). By using a colour mixture of any of the three kinds of copper phthalocyanine blue and I. C. Pigment Violet 23, that is a kind of dioxazine violet, light transmission between 500 and 550 nm is suppressed and the colour purity is improved. However, the light transmission in the desired blue range between 420 and 500 nm is also suppressed, causing insufficient brightness of the displayed images including the background. In the actual display operation, the light transmission in the desired blue range is reduced to from 70 to 80 % of those in the other colour ranges by a polarizer plate. Therefore, it has been required to increase the light transmission amount through the blue colour filter.

In view of the foregoing, it is an object of the invention to provide a blue colour filter, the transmittance thereof is high for the blue colour and low for the green colour. It is another object of the invention to provide an organic electroluminescent device that exhibits an excellent blue colour purity.

According to an aspect of the invention, there is provided a blue colour filter including: a photosensitive resin; and a dye containing at least a first cyanine dye described by the following structural formula (1).



(1)

Advantageously, the blue colour filter contains from 0.5 to 30 weight parts of the first cyanine dye with respect to 100 weight parts of the photosensitive resin.

blue material for image formation containing copper phthalocyanine blue. By combining the present colour filter and an organic EL element, the blue organic EL device according to the invention is obtained.

To describe in other words, the blue material used in the blue colour filter for image formation according to the invention contains a photosensitive resin and a blue dye mixed in the photosensitive resin. The main component of the blue dye is the cyanine dye described by the structural formula (1).

The blue dye used in the blue colour filter according to the invention contains the cyanine dye described by the structural formula (1). This cyanine dye is used alone or in combination with other dyes. Since the cyanine dye described by the structural formula (1) is very stable chemically and thermally, the blue colour filter containing this cyanine dye is very resistive thermally even when the blue colour filter is not formed by the pigment dispersion method. The cyanine dye described by the structural formula (1) may be used with a copper phthalocyanine blue pigment with no problem.

The blue material for image formation according to the invention includes a photosensitive resin and the cyanine dye described by the structural formula (1) as its main constituents. The mixing ratio of the cyanine dye is preferably from 0.1 to 40 weight parts. The cyanine dye described by the structural formula (1) and mixed as a main component suppresses the light transmission between 500 and 550 nm and improves the colour purity. The mixing ratio of the cyanine dye is more preferably from 0.5 to 30 weight parts with respect to 100 weight parts of the photosensitive resin. When the film thickness of blue pixels formed of the blue material for image formation on a substrate is from 1 to 20 μm as desired and the content of the cyanine dye described by the structural formula (1) is more than 30 weight parts, the light transmission in the range between 420 and 500 nm is also suppressed. When the content of the cyanine dye described by the structural formula (1) is less than 0.5 weight parts, the light transmission in the range between 500 and 550 nm is not suppressed sufficiently, and colour purity improvement is not attained at the film thickness between 1 and 20 μm. By mixing the blue dye to a photosensitive resin at a suitable mixing ratio as described later, the blue material for image formation of the invention is obtained.

trimethylol propane trimethacrylate, trimethylol ethane triacrylate, trimethylol ethane trimethacrylate, pentaerythritol diacrylate, pentaerythritol dimethacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, dipentaerythritol tetraacrylate, dipentaerythritol tetramethacrylate, dipentaerythritol hexaacrylate, dipentaerythritol hexamethacrylate, glycerol acrylate, and glycerol methacrylate; and acrylates of bisphenol epoxy such as 2,2-bis(4-hydroxy phenyl)propane and 9,9-bis(4-hydroxy phenyl)olefin. These compounds are used alone or in an appropriate combination.

A compound that works both as an alkali-developing resin binder and as a photo-polymerizing multifunctional cross-linking agent, that is a compound having a carboxyl group and such a group that facilitate development by an alkaline developing agent and an ethylenic unsaturated double bond in a molecule, is used for an organic resin binder. Such an organic resin binder is preferable to obtain a large solubility differences between the cross-linked portions exposed to the exposure light and the unexposed portions so that an excellent pattern of blue pixels may be obtained and to obtain a cured blue colour filter film that exhibits excellent thermal resistance and excellent alkali resistance.

The compound, that has a carboxyl group and such an alkali-developing group and a photo-polymerizing ethylenic unsaturated double bond, includes acid-addition products of epoxy acrylate or epoxy methacrylate obtained by reacting the hydroxy group of epoxy acrylate or epoxy methacrylate, obtained by reacting an epoxy compound and acrylic acid or methacrylic acid, with polybasic acid or with an anhydride of the polybasic acid.

The epoxy compounds used for the above described reactions include bis(4-hydroxy phenyl)ketone, bis(4-hydroxy-3,5-dimethylphenyl)ketone, bis (4-hydroxy-3,5-dichlorophenyl)ketone, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxy-3,5-dimethylphenyl)sulfone, bis(4-hydroxy-3,5-dichlorophenyl) sulfone, bis(4-hydroxyphenyl)hexafluoropropane, bis(4-hydroxy-3,5-dimethyl phenyl)hexafluoropropane, bis(4-hydroxy-3,5-dichlorophenyl)hexafluoro propane, bis(4-hydroxyphenyl)dimethylsilane, bis(4-hydroxy-3,5-dimethyl

The polybasic acid and the anhydride of the polybasic acid, which are reactive with the hyroxy group in the epoxy acrylate molecule or the epoxy methacrylate molecule, also include half-esterified compounds. The half-esterified compounds are obtained by reacting maleic anhydride with acrylate such as hydroxyethyl acrylate, having an alcoholic hydroxy group in the maleic anhydride portion of the copolymer, or with acrylate such as glycidyl methacrylate having an epoxy group in the maleic anhydride portion of the copolymer. The copolymers are obtained by co-polymerizing maleic anhydride and a monomer that co-polymerizes with maleic anhydride. The monomer that co-polymerizes with maleic anhydride includes ethylene, propylene, isobutene, styrene, vinyl phenol, any of their ether derivatives, any of their ester derivatives, acrylic acid, acrylate and acrylamide. The polybasic acid and the anhydride of the polybasic acid, which are reactive with the hyroxy group in the epoxy acrylate molecule or the epoxy methacrylate molecule, further include compounds obtained by reacting acrylic acid or methacrylic acid with the hydroxyl group in an acrylate copolymer having alcoholic hydroxyl groups. The acrylate copolymer is obtained by reacting acrylic acid, methacrylic acid, acrylate or methacrylate with acrylate such as hydroxyethyl acrylate having an alcoholic hydroxyl group.

The photo-polymerizing compounds having an ethylenic unsaturated double bond and a carboxylic group are not limited to those descried above. The photo-polymerizing compounds descried above are used alone or in an appropriate combination.

The photo-polymerization initiator and/or the sensitizer includes acetophenone compounds such as acetophenone, 2,2-diethoxyacetophenone, p-dimethylacetophenone, p-dimethylaminopropyophenone, dichloroaceto-phenone, trichloroacetophenone, and p-tert-butylacetophenone; benzo-phenone compounds such as benzophenone, 2-chlorobenzophenone and p,p-bisdimethylaminobenzophenone; benzoisoether compounds such as benzyl, benzoin, benzoin methyl ether, benzoin isopropyl ether, and benzoin isobutyl ether; sulphur compounds such as benzyl methylketal, thioxanthone, 2-chlorothioxanthone, 2,4-diethylthioxanthone, 2-methylthioxanthone, and 2-isopropylthioxanthone; anthraquinone compounds such as 2-ethyl-anthraquinone, octamethylanthraquinone, 1,2-benzanthraquinone, and 2,3-diphenylanthraquinone; organic peroxides

The blue material for image formation used in the blue colour filter according to the invention is prepared in the following way. A photosensitive resin solution is prepared by mixing an optically transparent photosensitive resin, a photo-polymerization initiator and a sensitizer at a predetermined ratio and by dissolving the mixture into a predetermined solvent. The photosensitive resin solution and a blue dye containing the compound described by the structural formula (1) as its main component are mixed at a desired ratio, resulting in a blue material for image formation. If necessary, the blue material is diluted so that a desired solid concentration may be obtained.

The blue material, thus obtained, is coated on a transparent substrate, such as a glass substrate, at a desired thickness. The blue material film is patterned by photolithography to form blue pixels. A polychromatic colour filter is manufactured by forming red pixels and/or green pixels using red material for image formation and/or green material for image formation before or after the blue pixel formation.

Finally, a polychromatic organic EL device is obtained by forming an organic EL element that works as a back light source on the colour filter.

Now the present invention will be explained hereinafter in connection with referred embodiments thereof.

First embodiment (E1)

Fabrication of a blue colour filter

An optically-transparent photo-polymerizing resin (259PAP5 supplied from Nippon Steel Chemical Co., Ltd.), containing 2 weight parts of a cyanine dye described by the structural formula (1) with respect to 100 weight parts of the solid component of the resin, is used for a blue material for image formation. The blue material for image formation is coated by spin-coating and dried, resulting in a blue material film. The resulting blue material film is 8 μm in thickness. The blue material film is exposed to the light from a high-pressure mercury lamp through a mask for obtaining a stripe pattern of 0.33 mm in line pitch and 0.12 mm in gap by contact exposure. A stripe pattern is formed by developing the exposed blue material film with alkaline aqueous solution. Then, by drying the developed stripe pattern, a blue colour filter having a tripe pattern of 0.33 mm in line pitch and 0.07 mm in gap is obtained.

are formed one by one without breaking the vacuum of the chamber. Table 1 lists the materials for the respective organic layers and the structural formulas thereof. The hole injection layer 5b is a copper phthalocyanine (CuPc) layer, 100 nm in thickness. The hole transport 5c is a 4,4-bis[N-(1-naphthyl)-N-phenyl amino]biphenyl (α-NPD) layer, 20 nm in thickness. The light emitting layer 5d is a 4,4-bis(2,2-dipheny vinyl)]biphenyl (PDVBi) layer, 30 nm in thickness. The electron injection layer 5e is a tris(8-hydroquinoline) aluminium complex (Alq) layer, 20 nm in thickness. The organic EL element emits blue light having a peak at 470 nm.

The conversion efficiency of the organic EL device fabricated as described above is measured. And, the x-and y-values of the CIE chromaticity coordinate are measured using a colour meter.

A reference organic EL device, not including any blue colour filter, is fabricated. The current value at that the reference organic EL device emits light at the luminance of 100 cd/m² is defined as a standard current. The luminance of the light, that the organic EL device including the blue colour filter emits at the standard current, is defined as a conversion efficiency.

Conversion efficiency (%) =
(Luminance of the organic EL device including the blue colour filter)/
(Luminance of the reference organic EL device)X 100 =
Luminance of the organic EL device including the blue colour filter

The CIE chromaticity coordinates are determined by feeding the standard current to the organic EL device and by measuring the blue light through the blue colour filter with a colour meter (MCPD-1000 supplied from Otsuka Electronics Co., Ltd.).

Table 2 compares the conversion efficiencies, the x-and y-values on the chromaticity coordinate and the transmittance values at the wavelengths of 470 nm and 500 nm of the blue colour filters according to the embodiments and comparative examples of the invention.

Table 2

	Conversion efficiencies (%)	CIE chromaticity coordinates		Transmittance (%)	
		x values	y values	470 nm	500 nm
E 1	35	0.13	0.10	87	59
E 2	32	0.12	0.09	87	59
C 1	40	0.16	0.14	66	67
C 2	15	0.12	0.10	73	33

<u>Second embodiment (E2)</u>

A blue colour filter (E2) according to a second embodiment is fabricated in the same way as the blue colour filter according to the first embodiment except that blue material for image formation according to the

The spectroscopic transmittance of the blue colour filter according to the comparative example 2 is measured and described by the curve d in Fig. 2.

An organic EL device is fabricated using the blue colour filter according to the comparative example 2. The conversion efficiency and the x-and y-values on the CIE chromaticity coordinate of the organic EL device according to the comparative example 2 are measured and listed in Table 2.

By comparing the measured values for the embodiments and the comparative examples, the following conclusions may be derived.

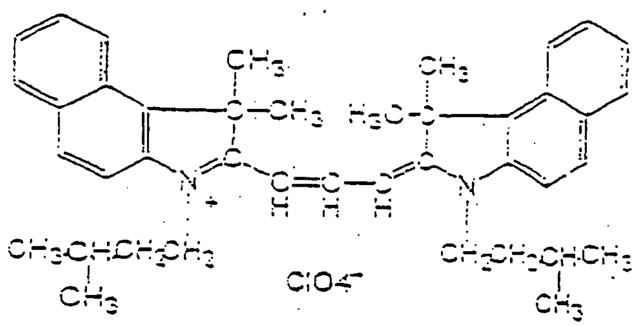
Referring now to Fig. 2, the blue colour filter according to the first embodiment has a transmittance peak at 450 nm, indicating that the blue colour filter according to the first embodiment contributes more to the blue colour purity than the blue colour filter according to the comparative example 1. The blue colour transmittance of the blue colour filter according to the first embodiment is higher than those of the blue colour filters according to the comparative examples 1 and 2, indicating that the blue colour filter according to the first embodiment exhibits an excellent energy conversion efficiency. The transmittance of the blue colour filter according to the second embodiment is low in the long wavelength range, contributing more to realizing a high colour purity as explained later.

Although better colour purity is obtained as the x-and y-values as the blue colour purity indexes are smaller than the NTSC hue (0.14, 0.08), the luminance of the transmitted light from the same light source is lower at smaller x-and y-values. The x- and y-values for the organic El devices according to the first and second embodiments are smaller than those of the organic El device according to the comparative example 1, confirming that the dye including the cyanine dye described by the structural formula (1) is effective for improving the blue colour purity. The y-value (0.09) of the organic El device according to the second embodiment, in that the cyanine dye described by the structural formula (2) is added, is quite near to the y-value (0.08) of the NTSC hue.

Higher luminance is obtained with increasing conversion efficiency. Although the x- and y-values for the organic El device according to the comparative example 2 are smaller than those for the organic El devices according to the first and second embodiments, the

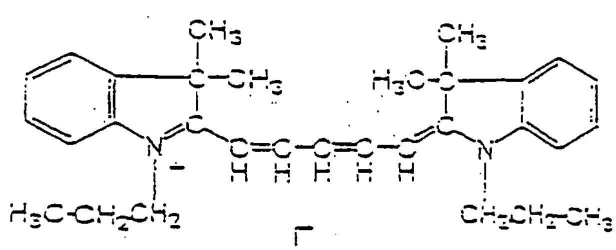
CLAIMS

1. A blue colour filter comprising:
a photosensitive resin; and
a dye containing at least a first cyanine dye described by the following structural formula (1).



(1)

2. The blue colour filter according to Claim 1, wherein said blue colour filter contains from 0.5 to 30 weight parts of said first cyanine dye with respect to 100 weight parts of said photosensitive resin.
3. The blue colour filter according to Claim 1, wherein said dye containing said first cyanine dye further contains a second cyanine dye described by the following structural formula (2).



(2)

4. The blue colour filter according to Claim 3, wherein the content of said second cyanine dye is from 0.5 to 1.5 weight parts with respect to 1 weight part of said first cyanine dye.

Application No:	GB 0009403.7	Examiner:	Miss M M Kelman
Claims searched:	1 to 12	Date of search:	19 July 2000

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C3K KAA C3V VBC

Int Cl (Ed.7): C08K 5/00, 5/3417; C09B 57/00; C09K 11/06; G02B 5/20; H05B 33/00 33/12, 33/14

Other: ONLINE: CAS-online, EPODOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB 2313921 A	INTERNATIONAL BUSINESS MACHINES	
A	EP 0723167 A2	MITSUBISHI CHEMICAL CORPORATION	
A	EP 0387715 A2	IDEMITSU KOSAN COMPANY LIMITED	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.